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STUDIES ON THE ESSENTIAL OILS OF THE PAKISTANI SPECIES OF THE FAMILY UMBELLIFERAE

Part XVII. *Heracleum candicans* (Eng. Cowparsnip. var. Morchar) Seed Oil

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The chemical composition of the essential oil of the fresh and mature seeds of *Heracleum candicans* collected from Murree and Kalam has been determined. The oil from the seeds of the respective localities obtained in 0.65% and 0.82% yields, is composed of α-pinene (0.27, 0.15%), *p*-cymene (0.82, 0 %), limonene (2.66, 0.15%), curcumene (0.23, 0%), β-bisabolene (0.23, 0%), cadinene (0.57, 0.64%), β-selinene (0, 0.21%), β-elemene (0, 0.17%), butyl butyrate (0, 0.15%), isobutyl-2-methyl butyrate (1.41, 4.45%), n-butyl isovalerate (1.26, 10.98%), n-hexyl-isobutyrate (2.21, 2.12%), butyl hexanoate (3.00, 1.13%), octyl acetate (4.50, 6.00%), hexyl-pentanoate (16.90, 3. 83%) amyl acetate (10.94, 19.57%), bornyl acetate (27.12, 21.45%), hexyl caproate (9.65, 8.67%), neryl acetate (0, 0.32%), linalool (1.04, 0%), santenol (0.57, 0%), capric acid (14.08, 0%), lauric acid (0.14, 14.0%), myristic acid (0,14.27%), palmitic acid (0, 4.21%) and santalic acid (0, 0.14%). By virtue of its fragrance the essential oil of the species holds good promise of being commercialised.

INTRODUCTION

Heracleum candicans has a wide distribution in the temperate regions of Asia and Europe. In Pakistan, it grows wild in Murree, Hazara, Chitral Dir, Swat, Gilgit and Kashmir. The plant is used, as a cure against some diseases of sheep and goats. Its seed increases the rate and amplitude of respiration and is used as stimulant. The plant raises blood pressure and stimulates the central nervous system. Its roots are used as incense. In some other countries the essential oil of the species is popularly known as *Heracleum* oil which is used in perfumery [1]. But the commercial importance of the oil of Pakistani species has not been realised so far.

Because of a rather pleasant fruity smell of the seed and as the plant can become an important raw material of the country, the chemistry of its essential oil has been investigated in detail.

EXPERIMENTAL

Material and Methods. Fresh and mature seeds of *H. candicans* were hand collected from Murree and Kalam. The oil was steam distilled according to the standard method [2,3]. The general methods used for these investigations have already been described in our earlier publications [2,3]. In addition, a time and temperature programmed GLC coupled with mass spectrometry was employed to analyse the oil.

Chromatography of the Oil. The essential oil was column chromatographed using silica gel as an adsorbent. The resolution of the oxygenated components consisting chiefly of a large number of esters, by this method proved ineffective. The ester were, thus, resolved and identified by GLC. The alcoholic constituents of the oil, recovered with 15% diethyl ether in n-hexane, were identified by IR and GLC comparison with their standard samples. However, due to the complex nature of the oil, its resolution by time and temperature programmed GLC/MS using a glass column (0.25″×6′) packed with 3% silar 5 cp and identification of the various constituents was made from the computerised data.

RESULTS

The percentage yield, physicochemical values and the chemical composition of the essential oils are recorded in Tables 1 and 2. Resolution of the essential oils recovered from the seed of Murree and Kalam by GLC is shown in Figs. 1 and 2 respectively.

DISCUSSION

The essential oil of *Heracleum candicans* is quite

Table 1. Yield and physicochemical values of the essential oil of *Heracleum candicans* seeds of two different localities.

	Oil recovered from	
	Murree seeds	Kalam seeds
Yield (%)	0·65	0·82
Colour	Yellowish	Yellowish
Specific gravity*	0·8510(32)	0·8634(25)
Refractive index*	1·4420(32)	1·4359(25)
Optical rotation*	—24°50′(32)	—13°52′(25)
Acid value	15·6	14·90
Ester value	260·12	240·30

*The temperature at which these parameters were determined are given in parenthesis.

Table 2. Composition of the essential oil of *Heracleum candicans* seeds of two different localities.

Oil from Murree seeds			Oil from Kalam seeds	
Peak No.		%	Peak No.	%
1.	α-Pinene	0.27	1. Butyl butyrate	0.15
2.	Isobutyl-2-methyl butyrate	1.41	2. α-Pinene	0.15
3.	n-Butyl isovalerate	1.26	3. Isobutyl-2-methyl butyrate	4.45
4.	*p*-Cymene	0.80	4. n-Butyl isovalerate	10.98
5.	Limonene	2.66	5. Limonene	0.15
6.	n-Hexyl isobutyrate	2.21	6. n-Hexyl isobutyrate	2.12
7.	Butyl hexanoate	3.00	7. Butyl hexanoate	1.13
8.	Octyl acetate	4.50	8. Octyl acetate	6.00
9.	Hexyl pentanoate	16.90	9. Hexyl pentanoate	3.82
10.	Amyl acetate	10.94	10. Amyl acetate	19.57
11.	Bornyl acetate	27.12	11. Bornyl acetate	21.45
12.	Linalool	1.04	12. Unknown (mol. wt. 196)	0.63
13.	Hexyl caproate	9.65	13. Unknown (mol. wt. 196)	0.24
14.	Unknown (mol. wt. 186)	1.10	14. Neryl acetate	0.32
15.	Santenol	0.57	15. Hexyl caproate	8.67
16.	β-Bisabolene	0.23	16. β-Selinene	0.21
17.	Curcumene	0.23	17. β-Elemene	0.17
18.	Capric acid	14.08	18. Santalic acid	0.14
19.	Cadinene	0.57	19. Unknown (mol. wt. 204)	0.58
20.	Lauric acid	0.14	20. Myristic acid	14.27
21.	Unknown (mol. wt. 172).	1.30	21. Cadinene	0.64
			22. Palmitic acid	4.21

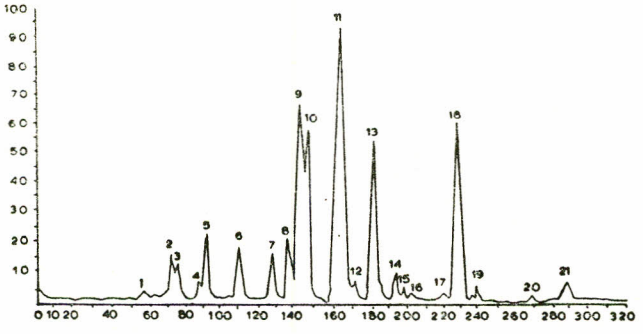

Fig. 1. Time and temperature programmed GLC of *Heracleum candicans* essential oil using 3% silar 5 cp. glass column (0·25″×6′)

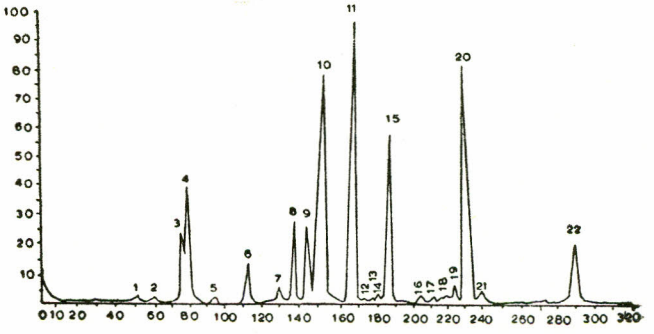

Fig. 2. Time and temperature programmed GLC of *Heracleum candicans* essential oil using 3% silar 5 cp. glass column (0·25″×6′).

pleasant in smell. The physicochemical characteristics and chemical composition of the two oils are almost identical. Both the oils contain relatively much smaller amount of hydrocarbons (less then 5%) and bigger proportion of esters. An oil of this nature is, therefore, much more valuable as an item of commerce.

The hydrocarbons are mixture of mono- and sesquiterpenes. The sesquiterpenes in the oil differ from each other; only cadinene being the common constituent. The presence of curcumens has been interpreted from the mass spectrometric data because we have not the standard sample of this sesquiterpene.

A survey of literature [4,5] reveals that mostly the essential oil obtained from the roots of *H. candicans* has been examined. However, Sarin and Kapoor [6] have reported the presence of some lactones in the essential oil recovered from the fruits of this species. On the basis of literature [4,5,6] survey the present work is considered to provide new information regarding the chemistry of *H. candicans* seed grown in Pakistan.

The oil is chiefly composed of a large number of esters (70–80%). The higher ester values of the two oils are in accordance with the results of chemical composition.

It is interesting to note that the oil contains a reasonable amount of fatty acids. Their identification is based on the GLC/MS data. The oils also contain a small amount of coumarins which are as yet to be identified.

The present studies indicate that the essential oil of *H. candicans* by virtue of its fragrance holds good promise of being used in perfumery. The species can

be commercialised on the basis of the good quality of its essential oil provided the species is tamed for cultivation. In this respect, our preliminary cultivation trials in these Laboratories have shown encouraging results.

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